

# Structural evidence for resonance-assisted O–H...S hydrogen bonding

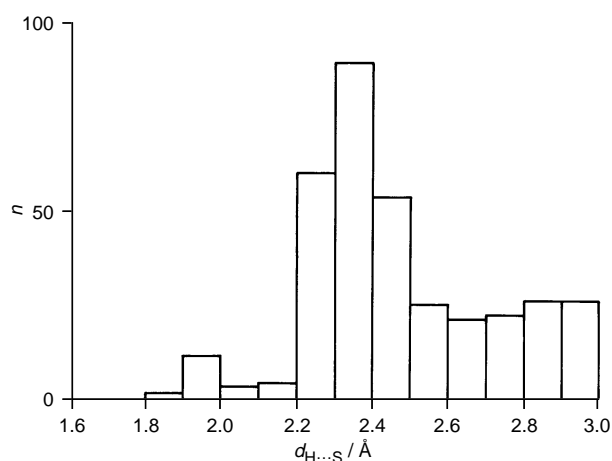
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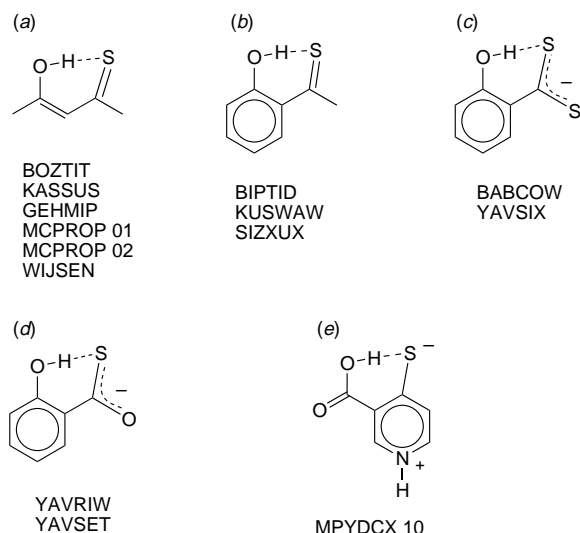
By far the shortest hydrogen bonds of the O–H...S type occur in monothio- $\beta$ -diketones and related substances (H...S distances 1.9–2.0 Å); it is shown with crystal correlation techniques that this very short hydrogen bonding is facilitated by resonance assistance similar to that occurring in the oxygen analogues.

Although O–H...S hydrogen bonds occur in many chemical and biological systems, they have been little investigated until today. The first comprehensive statistical analysis of intermolecular O–H...S hydrogen bond geometries was only recently published by Allen *et al.*<sup>1</sup> It is observed that in intermolecular hydrogen bonds, H...S distances are restricted to values  $> 2.2$  Å. In this present work, the database analysis of Allen *et al.* was followed, but intramolecular hydrogen bonds were also included.<sup>2†</sup> The distribution of H...S separations is clearly bimodal (Fig. 1). The large peak centred in the range 2.3–2.4 Å represents intermolecular hydrogen bonds, mostly of the type O–H...S=C.<sup>1</sup> The small peak centred in the range 1.9–2.0 Å was not evident in the previous study and represents exclusively intramolecular hydrogen bonds, which are apparently unusually strong. To discover what kind of interactions cause this prominent peak, the examples with H...S  $< 2.1$  Å were inspected individually. It was found that they are all structurally very similar and are formed in the structural fragments shown in Fig. 2 (numerical data given in Table 1).

The largest fraction of the data sample in Fig. 2 is composed of monothio- $\beta$ -diketones in the enol tautomeric form [Fig. 2(a)]. As an archetypal example, the structure of 3-mercapto-1,3-diphenylprop-2-en-1-one, which has been determined by neutron diffraction,<sup>3</sup> is shown in Fig. 3. Note that the covalent O–H bond length of 1.024(8) Å is appreciably elongated from the *ca.* 0.98 Å which is typically observed in moderate O–H...O hydrogen bonds,<sup>4,5</sup> indicating an interaction of considerable strength. For fragment (b) [2-hydroxybenzene-1-carbothioamides], IR spectroscopy shows redshifts of O–H



**Fig. 1** Distribution of H...S distances in inter- and intra-molecular O–H...S hydrogen bonds (for normalised H-atom position). The large peak centred at 2.3–2.4 Å is derived mainly from intermolecular hydrogen bonds and the small peak centred at 1.9–2.0 Å arises exclusively from intramolecular hydrogen bonds.



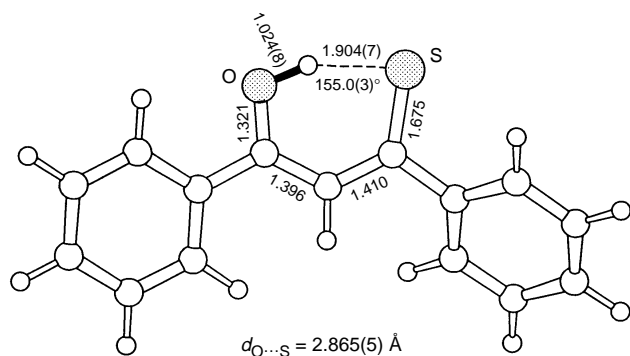
**Fig. 2** The crystal structures exhibiting intramolecular O–H...S hydrogen bonds with H...S  $< 2.1$  Å; (a) and (b) represent molecular fragments, (c)–(e) are drawn as they occur in the crystal

stretching frequencies of around  $450\text{ cm}^{-1}$  compared to free phenolic O–H, which are similar values as in the oxygen analogues.<sup>6</sup>

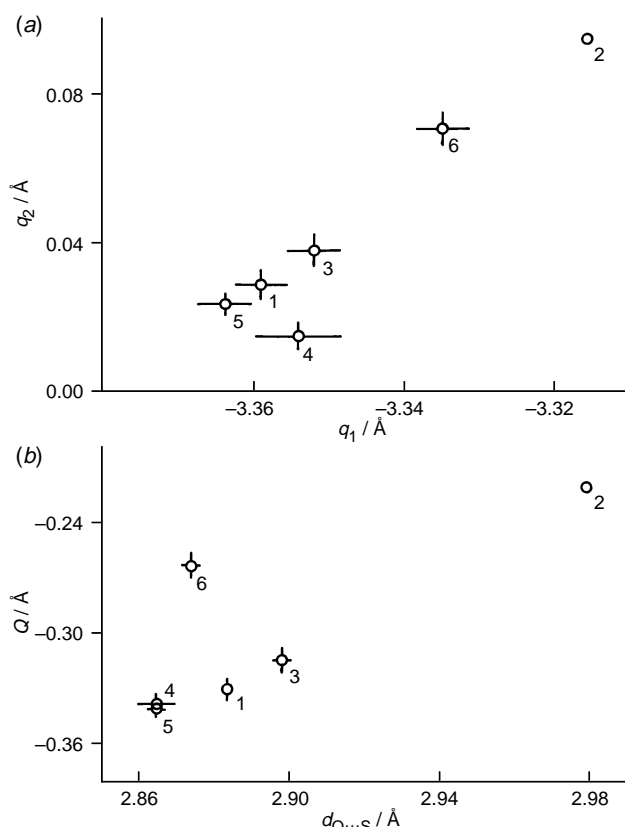
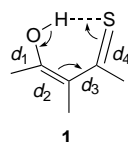
The short intramolecular hydrogen bonds in monothio- $\beta$ -diketones lead directly to the concept of resonance assisted hydrogen bonding (RAHB), which has been introduced by Gilli *et al.* to explain the observed strong hydrogen bonding in the oxygen analogue,<sup>7</sup> and was later put into a wider conceptual frame.<sup>5,8</sup> In this model, strong hydrogen bonding is possible if a suitably polarizable system of  $\pi$ -bonds allows charge flow through covalent bonds from the donor to the acceptor. Such systems are provided, for example, by conjugated double bonds. This cooperativity mechanism is well established for cyclic and

**Table 1** Crystal structures containing O–H...S hydrogen bonds with H...S distances  $< 2.1$  Å. All are intramolecular and resonance assisted (for X-ray structures based on normalised H-atom positions)

Compound	$d_{\text{H}\cdots\text{S}}/\text{Å}$	$d_{\text{O}\cdots\text{S}}/\text{Å}$	O–H...S (°)
BABCOW	1.92	2.848	156
BIPTID	1.95	2.886	159
BOZTIT	1.96	2.884	155
GEHMIP	2.04	2.979	159
KASSUS	1.98	2.898	155
KUSWAW	2.06	2.937	148
MCPROP 01 (neutron diffr.)	1.90	2.865	155
MCPROP 02	1.93	2.865	157
MPYDCX 10	1.94	2.868	157
SICXUX	1.94	2.904	167
SICXUX	2.00	2.919	154
WIJSEN	1.97	2.874	153
YAVSIX	2.01	2.891	149
YAVRIW	1.88	2.847	165
YAVSET	1.97	2.882	153



**Fig. 3** Molecular structure of a monothio- $\beta$ -diketone determined by neutron diffraction: mercapto-1,3-diphenylprop-2-en-1-one<sup>3</sup>



**Fig. 4** (a) Correlation of the parameter  $q_1$  ( $= d_1 - d_4$ ) and  $q_2$  ( $= d_3 - d_2$ ). (b) Correlation of  $Q = q_1 + q_2$  with the hydrogen bond distance  $O...S$ . The observed correlations imply that the arrangement in **1** is in fact a resonant cycle.<sup>6</sup> Note that a value of  $q_2 = 0$  corresponds to complete  $\pi$ -delocalisation of  $C=C-C$ . Error bars are included where standard errors of bond lengths were given in the original publication. Data are identified as **1**: BOZTIT. **2**: GEHMIP. **3**: KASSUS. **4**: MCPROP01. **5**: MCPROP02. **6**: WIJSEN.

non-cyclic  $O=C-C=C-O-H$  systems and for related heteronuclear cases with  $N-H$  donors,<sup>9</sup> and has even been postulated for  $C-H$  donors.<sup>10</sup> Since it has not been investigated as yet for sulfur acceptors, the mechanism is looked at more closely here.

If the RAHB model is applicable to the monothio- $\beta$ -diketones **1**, the situation should exactly parallel the oxygen

analogue, as is shown below. Because of the hydrogen bond, the  $O-C$  and the  $C-C$  bonds gain some double bond character and are shortened, whereas the  $C=C$  and  $C=S$  bonds lose part of their double bond character and are lengthened. To see if this is more than a suggestion, and if the hydrogen bond arrangement in fact represents a resonant cycle, it is necessary to perform geometrical tests. There are several ways to quantify  $\pi$ -system delocalisation; to make comparison easy, the formalism used by Gilli *et al.*<sup>6</sup> is also used here. It is obvious that in RAHB of increasing strengths, the bond length  $d_1$  reduces and  $d_4$  increases; since  $C=S$  is longer than  $O-C$ , this means that the difference  $q_1 = d_1 - d_4$  is negative and becomes more negative with increasing hydrogen bond strength. The difference in the  $C-C$  and the  $C=C$  bond lengths,  $q_2 = d_3 - d_2$ , is positive and decreases with increasing hydrogen bond strength. In the case of total  $\pi$ -delocalisation at  $C=C-C$ ,  $q_2$  becomes zero. If the arrangement as a whole is a resonant cycle, there must be a correlation between the parameters  $q_1$  and  $q_2$ . Furthermore, the  $\pi$ -delocalisation must increase with reducing hydrogen bond distance, so that  $q_1$ ,  $q_2$  and their sum  $Q = q_1 + q_2$  must correlate with  $O...S$  (or  $H...S$ ). The corresponding correlation plots for the monothio- $\beta$ -diketones are shown in Fig. 4. Despite the limited amount of data the correlations are sufficiently clear to show the anticipated trends [the single outlier in Fig. 4(b) is unexplained upon inspection]. This is conclusive evidence that the mechanism of resonance assisted hydrogen bonding is operative in this fragment.

The amount of data for the arrangements in Fig. 2(b)–(e) is insufficient for statistical analysis, but the structural and electronic similarities immediately suggest that they also represent decent RAHBs, which for arrangements (c)–(e) even contain a contribution of charge assistance.<sup>5</sup>

The arrangements in Fig. 2 represent by far the shortest  $O-H...S$  hydrogen bonds known, about 0.4 Å shorter than typical intermolecular hydrogen bonds. This circumstance is readily explained by the operation of resonance effects within the cyclic fragments, *i.e.* by resonance assisted hydrogen bonding which is analogous to that in  $\beta$ -diketones.<sup>7</sup> The general importance of this concept<sup>5,7</sup> is thereby further emphasised and its applicability for heteronuclear hydrogen bonds is confirmed. The other mechanisms that can produce strong hydrogen bonds, in particular charge assistance,<sup>8</sup> are not apparent in the pure form in the currently available structural data for  $O-H...S$  hydrogen bonding.

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## Notes and References

- \* E-mail: steiner@chemie.fu-berlin.de
- † Database analysis: Cambridge Structural Database,<sup>2</sup> June 1997 update with 167 797 entries, ordered and error-free organic crystal structures with  $R$  values  $< 0.08$  and H-atom positions normalised. The examples in Fig. 2 were individually inspected using the original publications.
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